Table of Contents

Page

1 Introduction

Aluminum is one of the most versatile materials available today that can meet the demanding requirements of tomorrow's products. Its light weight, high strength, and corrosion resistance make it ideal for applications in automobiles and trucks, rail, aerospace, containers, construction, electric transmission, and infrastructure. When used in transportation vehicles, it can greatly increase the energy efficiency of our Nation's transportation sector. Aluminum's success in recycling has also made it a model for sustainable materials. However, the production of primary aluminum continues to be quite energy intensive. Furthermore, the use of carbon anodes in the smelting process generates undesirable carbon dioxide and perfluorocarbons.

While past technology improvements have greatly increased the current efficiency of aluminum cells up to 96%, the industry continues to pursue research to increase energy efficiency, improve productivity, and reduce emissions in primary aluminum production. In particular, the international aluminum community has pursued the development of non-consumable, or inert, anode technology for many years. If successful, this technology would have clear advantages over conventional carbon anode technology, including the following "best estimates":

- energy efficiency increases of up to 25% (when coupled with a stable, wetted cathode)
- operating cost reductions of up to 10%
- greenhouse gas emissions reductions of 7 million metric tons of carbon equivalent in the United States
- productivity increases of up to 5%

This technology is particularly relevant today as nations around the world look for technologies that can help reduce emissions of greenhouse gases without compromising economic growth and product quality.

Although not absolutely required, retrofit capability is highly desirable of any new inert anode technology. The technology holds great promise for brownfield capacity additions and retrofit applications in North America. However, the largest impact may ultimately be realized in the application of inert anode technology to greenfield aluminum smelting projects throughout the world. Undoubtedly, the latest, most advanced technology will be adopted for any greenfield smelter project.

Why Inert Anodes?

One of the largest opportunities to lower the energy requirements and costs of primary aluminum production is through the use of advanced electrolytic cell designs. Advanced cell technology has been one of the top research priorities among aluminum companies for several decades. The industry affirmed the need for this technology during the *Aluminum Industry Technology Roadmap Workshop* held in November, 1996. Leading industry experts selected the development of advanced anode and cathode technology as its highest-priority R&D objective for primary production over the next 20 years. Research activities in this area should focus on the development of new materials for inert anodes and wetted cathodes, processing methods for these materials, and experimental design for materials selection.

The electrolytic production of aluminum is very energy intensive. In fact, electricity accounts for about one-third of the cost of production and is one of the key factors behind product affordability. The largest technical challenge to improving the energy efficiency of electrolysis is the development of a non-consumable, or inert, anode. Inert anode technology, coupled with that of stable, wetted cathodes, offers the greatest opportunity to improve cell energy efficiency and lower primary aluminum production costs. The technology also has significant environmental benefits because it eliminates the emissions of carbon dioxide and perfluorocarbons (particularly carbon tetrafluoride) associated with consumption of the carbon anode. In addition, improving cell energy efficiency will lower overall energy requirements, thereby reducing the emissions of greenhouse gases that may have resulted from primary electricity generation.

However, with inert or non-consumable anodes, the electrode reactions differ from those with carbon anodes. On carbon anodes the oxygen of alumina is discharged but reacts with the carbon and forms carbon dioxide, which decreases the decomposition potential by about a volt. Such depolarization does not occur on inert anodes. Oxygen is evolved at the standard decomposition voltage. There is some evidence that the anode overpotential is somewhat less with oxygen formation but not enough to fully compensate for the one volt depolarization.

If successfully developed and applied, inert anode technology could have significant energy, cost, productivity, and environmental benefits for the aluminum industry worldwide. When combined with other advances in electrolytic cell design, such as wettable cathodes, the technology should achieve even greater benefits. These benefits include an expected 25% reduction in the energy required for reduction of alumina to aluminum and, most importantly, elimination of the carbon anode plant. Although inert anodes will require a production facility, the industry's best guess is that the facility will be offsite and not require aluminum industry capital. The inert anode production facilities are expected to be less polluting than carbon anode plants.

The ability of inert anode technology to reduce emissions of greenhouse gases is also of great interest to the industry. In the United States alone (using the 1996 primary aluminum production rate of 3,577 thousand metric tons), the application of inert anodes could potentially eliminate 5 million metric tons of carbon dioxide emissions and more than 2,500 metric tons of perfluorocarbon emissions. When converted to carbon equivalent, the total reduction in greenhouse gases would be nearly 7 million metric tons. Worldwide, this potential translates to a reduction of greenhouse gas emissions by nearly 40 million metric tons (carbon equivalent). Additional reductions in emissions would result from the improved operation of the cell itself.

A Framework for Technology Development

Guided by the Technical Advisory Committee of The Aluminum Association, leading North American aluminum producers have collaborated to establish a framework to guide the development of any new inert anode technology. In this framework, the industry has developed a consensus on the required performance characteristics and development requirements of the technology. These characteristics and requirements represent a unique consensus by nine leading North American primary aluminum producers (see Appendix A). The framework is a logical extension of the aluminum industry technology roadmap and is intended to provide the basis for guiding and judging new inert anode concepts. The industry anticipates that the framework will also serve to accelerate research efforts in this area by aligning the different segments of the research community toward a clearly defined goal.

The initiative being taken by the aluminum industry is very timely considering the increased interest in advanced industrial technologies that can reduce greenhouse gas emissions. Recently, the Clinton Administration proposed additional funds for research and development and tax initiatives to encourage the development of new technologies to spur energy efficiency and reduce emissions of carbon dioxide and other greenhouse gases. Additional incentives are promised for industries that take early action.

Rather than attempting to select a specific technology winner, the aluminum industry has taken the unique approach of developing the framework by which inert anode development should proceed. This approach recognizes an important distinction: aluminum companies appear best able to identify their technology performance requirements while the academic and research community appear best able to generate innovative technology solutions. The framework has two main parts:

- the technical performance characteristics
- the technology development and scale-up pathway

Key technical performance characteristics for successful operation of an electrolytic cell using inert anode technology are quantified and discussed. The sequence of generic development steps for any new inert anode technology are identified, and their critical components explained. In addition, the document includes in-depth discussions of the potential benefits of inert anode technology and the key technical challenges that it must overcome.

2 Potential Benefits

If successful, non-consumable, or inert, anode technology could yield significant energy, environmental, and cost benefits. As shown in Exhibit 2-1, the benefits are expected to fall into the following categories:

- Cost/Productivity
- Process Simplification/Control
- Energy Reduction
- Elimination of Greenhouse Gases
- Other Environmental Benefits

The benefits shown in Exhibit 2-1 are actually the *requirements* that the aluminum industry has developed for non-consumable anodes. While no single new technology must meet all of these requirements in order to be considered successful, the degree of success may be measured by how many of the requirements are indeed fulfilled.

To measure the benefits of the new anode technology (used in combination with wettable cathode technology), a comparison will have to be made not just against current technology but also against a cell operating with conventional anode technology and potential wettable cathode technology. This will yield the relative benefits and costs of technology improvement.

All of the projected benefits are discussed below in turn, although they will become somewhat less important if the government imposes restrictions that *require* reductions in CO_2 emissions because the economics of the proposed technology will become less important. Nevertheless, the industry has determined that an aggressive effort should be made to develop non-consumable anode technology aimed at achieving a number of important benefits such as energy reduction, as well as the reduction of greenhouse gas emissions.

Cost/Productivity

An important requirement is to lower the overall cost of a new anode below that of conventional carbon anodes, which is usually $110 to $120 per tonne. Other potential benefits include increases in space utilization and production per unit volume (consistent with the constraints of the heat balance of the cell). The new anodes should reduce labor requirements during operations as well as overall operating costs.

Exhibit 2-1. Potential Benefits Expected/Required from Inert Anodes

(– = Greatest Industry Benefit; **k** = Greatest National/Global Benefit)

Cost/ Productivity	Process Simplification/ Control	Energy	Greenhouse Gas Emissions	Safety & Health	Other Environmental Benefits
Lower anode cost Increased space utilization More production per unit volume Less operating labor Opportunity to retrofit to work with carbon cathodes Higher metal quality - no dissolution of anode components Increased flexibility in cell design –	Eliminate carbon plant –––––––––– ––– Many fewer anode changes Control system changes - how to deal with fixed plane anode and moving-plane cathode Dimensionally stable flat bottom - better control of anode-cathode distance (ACD)	More thermally efficient cell Lower heat losses Energy saved from elimination of carbon anode production Potential for lower ACD when combined with wettable cathode –	Reduce/eliminate CO_2 emissions **k k k k k k k k k k** **k k k** Reduce/eliminate PFC emissions **k k k**	Fewer anode changes Improved industrial hygiene	Eliminate/reduce polycyclic aromatic hydrocarbons/ polycyclic organic matter Eliminate emissions of carbonyl sulfide Eliminate dry coke scrubbers and anode paste plant - also eliminate scrubbers from bake ovens Reduce spent pot liner - possible if combined with new cathode technology Reduce hydrogen fluoride (HF) emissions

Additional requirements of the new anodes are that they eliminate dissolution of anode components into the metal, thereby reducing levels of metal contamination and improving metal quality compared with the use of carbon anodes. A very desirable outcome of applying the new technology would be increased flexibility in the design of electrolytic cells. It is also anticipated that the new anodes will be retrofittable to cells using current (carbon) cathode technology in order to eliminate the high capital costs involved in the existing smelter infrastructure.

Process Simplification/Control

Probably the most important result of non-consumable anode technology is that it eliminates the need for the carbon plants currently used to manufacture carbon anodes. This benefit has been judged by the industry to be the single most important benefit of the technology to industry.

New anodes would be expected to have a much longer lifetime than carbon anodes, requiring far fewer anode changes. Control-system changes would be expected, although the precise nature of these changes is not yet clear. For example, if conventional cathodes were still being used, a system for operating the cell with a fixed-plane anode and a moving-plane cathode would be needed. It is not known if there would be the same response to the alumina concentration/voltage curve under these circumstances, presenting an argument in advance for a better control system. Issues still remain related to the solubility of oxygen in the electrolyte and may affect process simplification.

The dimensionally stable flat bottom of the new anode would enable better control of the anode-cathode distance (assuming that an algorithm to compensate for the rising metal were developed). In general, the technology should provide more precise anode-cathode distance control, although it would not eliminate problems with magnetics in regard to the molten metal.

Energy

The enthalpy required to sustain the reduction process has been established. However, in terms of containing multiple electrodes in a large cell, a bigger, better-built cell system allows better insulation. The electrolytic cell system with the new anode should have improved thermal efficiency, in part through lower heat losses (due to better insulation) and perhaps also from narrowing the anode-cathode distance (ACD).

It is uncertain at this time if a reduction in ACD will be sufficiently great to yield energy benefits if the anode is used against a conventional cathode. The potential for energy savings definitely exists for the combination of non-consumable anodes and dimensionally stable cathode technology. Some of this depends on the activity of the oxygen present in the cryolite bath versus the reactivity of the carbon dioxide, which is not completely understood at this time. However, an inert anode would add another dimension to wettable cathode technology, giving the potential for energy efficiency. Energy savings should also be realized from the elimination of carbon anode production, particularly anode baking.

Greenhouse Gas Emissions

The two categories of greenhouse gases that will be reduced or eliminated by the use of non-consumable anode technology are

- carbon dioxide (CO_2) and
- perfluorocarbons (mainly CF_4 but also C_2F_6).

Process-related CO_2 emissions from the consumption of the carbon anode will be eliminated. Emissions of perfluorocarbons will be eliminated because the inert anode does not contain carbon. The reduction in emissions of these gases has been noted by the industry to be the most important national or societal benefit of non-consumable anode technology.

Other Environmental Benefits

There should be fewer emissions of other compounds following adoption of new anode technology. These compounds include

- polycyclic organic matter (POM) generated during anode manufacture and consumption;
- hydrogen fluoride (HF) generated during electrolysis, anode effects, and anode replacement; and
- carbonyl sulfide (COS) generated during electrolysis.

The reduction in hydrogen fluoride emissions could result from the system being better contained (more tightly sealed) as well as from the reduced turnover in anodes.

In one sense, the new anode technology can be seen as an alternative control device for these types of emissions. The anode paste plants used to produce carbon anodes can be eliminated in many cases, along with the dry coke scrubbers used to collect POM emissions from anode paste production. The use of scrubbers for controlling POM emissions from anode bake furnaces (typically, dry alumina scrubbers) can also be eliminated.

A possible additional benefit of combining non-consumable anode technology with wettable cathode technology would be a reduction in the amount of spent potliner that is generated, although this is somewhat speculative.

Health and Safety

The reduced number of anode changes associated with non-consumable anode technology would have important benefits related to safety and industrial hygiene as well as the other advantages already described. Many of the items listed in other categories can also be considered as health and safety benefits.

3 Performance Targets

A number of performance criteria or targets have been defined for inert anode technology and then screened to determine their level of importance to the technology's success. Two sets of performance targets have been defined:

- Essential (first-tier) targets
- Beneficial (second-tier) targets

The "essential" or first-tier targets are primarily technical criteria that absolutely must be met by the technology. They can be considered a screening mechanism through which a technology must pass before the second-tier targets are applied. These second-tier or "beneficial" targets are characteristics that are desirable but not absolutely necessary for the technology to succeed.

An economic analysis will be required once a material passes the first-tier criteria, and becomes an ongoing process that is carried out to increasingly detailed levels as the research progresses. During the first stage of a project, a gross analysis is conducted at the global level.

The criteria discussed in this section actually apply to an inert anode *system.* Since the industry is not ruling out the use of protective agents or coatings, there may be various ways to achieve the desired technology. For example, a self-passivating agent used to coat a carbon anode may represent an alternative inert material.

The performance targets given in the *Aluminum Industry Technology Roadmap* still apply to the overall anode system. These targets called for an energy consumption of 13 kWh/kg of aluminum produced for a retrofit cell and 11 kWh/kg of primary aluminum produced as the long-term goal.

Exhibit 3-1 shows the categories of performance targets that were identified by participants and the quantitative or qualitative target or metric for each that should be met by inert anodes.

Essential Targets

The essential characteristics for anodes are electrochemical and thermodynamic stability, electrochemical behavior, electrical conductivity, mechanical properties, oxidation, metal quality,

Exhibit 3-1. Performance Targets for Inert Anodes

Essential (1st Tier)	
Criterion	**Target for Inert Anode**
Electrochemical and Thermodynamic Stability	Erosion rate of <10 mm/yr with current density (0.8 amps/cm^2)
Electrochemical Behavior (Current Density)	Polarization voltage of <0.5 volts at 0.8 amps/cm^2
Electrical Conductivity	Voltage (continuous) drop no worse than with carbon anode - bus to electrolyte
Mechanical Properties	Sufficiently robust to survive in normal plant conditions - must withstand cell vibrations - must support its own weight - must maintain mechanical integrity - must not suffer from thermal shock - must survive in normal bath - must handle heat-up from room to operating temperature range of 930ºC - 1100ºC
Oxidation	Stability in oxygen at 1,000EC - should not spall - may be a higher/lower operating temperature
Metal Quality	No worse than today's quality - #0.1% Fe, 0.2% Si - meets today's market standards
Environmental and Safety Acceptability of the Material	Eliminate beryllium, chromium, radioactive and EPA-defined hazardous materials

Beneficial (2nd Tier)
Criterion
Health and Safety
Economics
Net Energy
Opportunity for Retrofit
Potential for Bath Chemistry Modification
Other Cell Construction Materials
Thermal Conductivity
Porosity
Positive Influence on Cathode Life

and environmental and safety acceptability of the material. The interconnections between many of these characteristics are mentioned in the appropriate subsections that follow.

Electrochemical and Thermodynamic Stability

The inert anode material must be electrochemically and thermodynamically stable, with electrochemical stability referring to the entry of the material matrix into the electrolyte.

Stability can be both calculated and measured; it is the ? G (Gibbs free energy of formation) required to carry out the reaction and any other competing potentials (e.g., contaminants like copper or iron). Some of the considerations of the new system are as follows:

- the synergism between the components of the new system is significant
- the target is thermodynamic stability in the electrolyte at operating temperatures

- the specific metric is the projected lifetime based on the erosion rate due to the electrochemical and thermodynamic stability
- the anode material must have a lower free energy of formation than the electrolyte in which it is placed

Past research efforts have tended to overlook two critical points:

- aluminum and sodium are soluble in the cryolite bath, which can lead to the formation of a concentration and diffusion gradient in the cell that can interact with the electrode
- aluminum and sodium confer electronic conductivity upon the electrolyte

The rate of oxidation of carbon to CO_2 in the cryolite bath is so great that there is never an electronically conducting interface in current carbon anodes. Given this situation, tests of new systems should include saturation of the test cell with aluminum or sodium to show that there are no excursions in voltage.

Stability measurements must include a metric for predicting when a material performs well enough to qualify moving ultimately to a five-year test. "Erosion rate" has been chosen as the criterion for measuring stability; metal quality (discussed later) is also a key indicator of anode performance. The specific target is **an erosion rate of less than 10 mm/year**, which contains some slack for adjustments to the bath. This has to be met under conditions of current flow (at the nominal or conventional current density of 0.8 amps/cm^2). This target is considered a "flag", and will not limit the research at the earliest stages because the erosion rate will still be unknown. However, if the erosion rate is much greater than this target, the industry will become somewhat cautious about the material. Any inert anode material developed during earlier investigations should meet this criteria or be ruled out for further consideration.

Electrochemical Behavior

The current density capability/capacity of the inert anode is a major component of electrochemical behavior, conventional anodes tending to operate at approximately 0.8 amps/cm^2. Specifically, the polarization voltage, which must be added to the 2.2 volts alumina decomposition voltage, must be kept to a minimum. The performance criterion defined is a **polarization voltage of less than 0.5 volts at 0.8 amps/cm^2**.

Electrical Conductivity

The new system must pass the electrical current from the connecting busbar to the actual double layer in the electrolyte on a continuous basis at a reasonable cost, while avoiding a conductivity problem at the interface between the busbar and the top end of the anode. In present cells, the voltage drops in the anode are on the order of 0.25 to 0.45 volts. Because the nature and thickness of the new material are unknown, the anode should have a voltage drop no greater than in the present cell, or else there is no gain in efficiency.

The new material also must be continuously conductive over the life of the anode. This conductivity should be available from extremely short time intervals, measured in microseconds, to long time periods of hours and days. The metric used to measure this conductivity is voltage drop across the material from bus to electrolyte. This must be based on the actual connections, which are unknown at this time. The material must behave like carbon in a reproducible way, with a **total voltage drop that is no worse than can be achieved with carbon at the current densities used today with carbon anodes**.

Mechanical Properties

The inert anode material must meet the following criteria:

- **must be sufficiently robust to survive and maintain structural integrity under standard plant operating conditions**
  - must not undergo thermal shock,
  - must hold its own weight
  - must withstand vibrations that occur in a normal cell (e.g., tapping, bumping).

In terms of thermal shock, the material must be able to survive in the molten cryolite bath and withstand temperatures ranging from room temperature to an operating temperature of 930°C to 1100°C. Thermal shock also relates to the coefficient of thermal expansion and the capacity of the material to be heated up over a period of time without spalling.

Other issues include mechanical integrity, stress rupture characteristics, and cracking; exposure tests should be conducted to reveal any internal cracking of the proposed anode material.

Oxidation

Oxidation resistance is related to electro/thermal stability and the lifetime of the anode. Oxidation occurs in present systems when the carbon comes in contact with electrolyte, CO_2, air, and crust. Since any new material in a retrofit application will have to pass through ambient air and the crust, to make contact with fluoride vapors, oxygen, liquid fluoride, heat, and crust, the material must be resistant to oxidation to ensure the quality of the molten metal. In addition, some of the material could convert to the vapor phase and get into the scrubber system, returning via the dry scrubber (although many of the issues with fluoride vapors should be taken care of with the stability in the molten electrolyte). The actual performance criterion is that **the material should not spall in oxygen at 1,000°C**. While it is acknowledged that operating conditions for baths may actually be lower than 1,000°C, an anode is likely to be exposed to temperatures approaching 1,000°C sometime during its life.

Metal Quality

The quality of the aluminum metal produced is related to electrochemical and thermodynamic stability of the anode material. The issue of metal quality is important enough to rate its own category. The criterion for metal quality is that it must be no worse than the quality of present-day metals. The inert anode may be made out of new metals that are not present in today's systems, but must last under practical conditions and not dissolve into the molten metal. By extension, it must be shown that the aluminum produced will be viable in the marketplace, meeting today's selling standards. The metal can become contaminated with almost any element at concentrations of up to 0.1 percent before the quality of the hot metal is affected; specific limits include concentrations of 0.1% iron and 0.2% silicon.

Environmental Safety and Acceptability of the Material

The criterion in this category is that the inert anode system should contain nothing from EPA's hazardous list (e.g., no beryllium, no chromium), and no radioactive materials.

Beneficial Targets

The "beneficial" or second-tier targets are related to economics, net energy use, opportunity for retrofits, potential for modifying the bath chemistry, other cell construction materials, thermal conductivity, porosity, influence on cathode life, and health and safety. Unlike the "essential" criteria, specific performance targets have not been defined for second-tier criteria. Comments on each of these targeted areas are presented below.

In some cases, educated guesses of the value of some of the "beneficial" criteria must be made in order to do an energy and economic analysis of the technology. The accuracy of these estimates will be improved, however, by applying the knowledge gained from establishing the "essential" criteria for the technology.

Economics

One purpose of this roadmap is to develop a screening mechanism for evaluating proposals for R&D projects. Therefore, strict economic requirements will not be placed on a proposed technology until its technical feasibility has been investigated. While it is difficult to translate all the technical factors into an economical package, and there is no targeted cost, the industry is unlikely to pursue a technology that is not cost-effective. On the other hand, the technology could still be viable even with varying economics, or some benefits of using the new technology may be more valuable in the future than they are today. Even with higher metal costs, a technology may be viable in certain regulatory climates in the future.

Net Energy

Net energy savings are required for the inert anode system, although the value of the savings will depend on the design of the cell, which is unknown at this point. It is very difficult to talk about net energy savings when considering the stable anode *alone*; the system boundary must be expanded.

Opportunity for Retrofit

The ability of the inert anode to be retrofitted to current cells is considered beneficial but not essential.

Potential for Bath Chemistry Modification

The potential for bath chemistry modification refers to the impact that the inert anode technology will have on the composition of the electrolyte. The performance criterion is that the technology should work with existing bath technology, at least as a starting point. The potential for electrolyte modification is a side benefit but not an absolute necessity.

Other Construction Materials

Other construction materials include insulators that will tolerate the medium in which the inert anode is expected to operate. A need for appropriate materials should not preclude the research community from pursuing a new anode technology that meets the first-tier criteria.

Thermal Conductivity

The thermal conductivity has to be such that the cell can operate, and must operate at an economical current density without releasing more heat than is generated within the system. Since the issue of thermal conductivity has to do with cell design, it may be possible to reconfigure the design to overcome thermal issues (for example, a high conductor could be backed up with an insulator or a cover).

Porosity

Any porosity will be detrimental to longevity and the permanence of the anode matrix, although it is not considered an "essential" criteria. Ideally, however, the porosity of the anode against O_2 and AlF_3 should be zero.

Influence on Cathode Life

If an inert anode technology reduces the life of a cathode significantly, the technology will face an uphill battle to be accepted. Unfortunately, any impact on cathode life will not be obvious in the early stages of research.

Health and Safety

Health and safety issues are essential but nebulous, especially when trying to define them for researchers. The category of environmental acceptability of the material was expanded to link it with safety (see "Essential Targets"); forbidden materials include heavy metals and hazardous compounds such as beryllium and chromium.

4 Technical Barriers

A number of critical technology barriers prevent the aluminum industry from achieving the targets it has identified for inert anode technology, as shown in Exhibit 4-1. In a sense, these challenges represent the difference between present-day carbon anode technology and the current state of non-consumable anode technology. The barriers/challenges have been organized into the following categories:

- Anode Materials
- Basic Knowledge
- Measurement/Evaluation/Analysis
- Systems

Both the “essential” and the “beneficial” criteria discussed in Section 3 have been considered in defining these barriers. In addition, the scope of the barriers is not limited to retrofit technology, although the industry recognizes that inert anodes will primarily be used in retrofit applications.

Anode Materials

Some of the most critical barriers to the success of inert anode technology exist because a “viable” material for fabricating the anodes has not yet been demonstrated. (Viable refers to the durability and longevity of the anode in keeping its initial thermal and chemical properties.) The industry feels that not enough material systems have been empirically investigated or characterized for their applicability to inert anodes. Too few composites or alloy-type materials have been studied in comparison to single compounds, although this may be warranted because the more complex materials present issues related to material life, conductivity, contamination, and durability.

Currently, major challenges include insufficient knowledge of the fabricability of candidate materials in large sizes, and the inability to scale up the fabrication processes. Many of the potential materials investigated in the past have never been produced on a large scale.

Other materials barriers include the inability to achieve adequately high erosion or wear characteristics at the frozen crust-electrolyte interface, and the need for defining a screening test for these characteristics.

Exhibit 4-1. Critical Technology Barriers Preventing Attainment of Targets

(M = Most Critical Barrier; • = Next Most Critical Barriers)

Anode Materials	Basic Knowledge	Measurement/ Evaluation/Analysis	Systems
Not enough knowledge of fabricability of candidate materials in large sizes - inability to scale-up fabrication process	Lack of understanding of process and models to understand it	Have not tested anode materials in continuous operation rather than short runs (anode durability issue) •	Ability to keep total cell voltage same or less than today's cells at same current density • • • • •
Have not yet seen demonstration of a viable anode material M M M M M M M M M M M • • - durability - longevity of anode keeping its initial thermal and chemical properties	Not enough understanding of the activity of O_2 vs. CO_2	Cost and time of demonstrating new materials	Ability to retrofit new anode to existing technology • •
Not enough anode material systems have been empirically investigated •	Lack of knowledge of anode reaction responses to bath chemistry • •	Have not evaluated worthiness of inert anode concept based on best extrapolated technologies M •	Lack of computer modeling that incorporates less-conventional materials and structures • • • - lack of good up-front simulation tools
Not enough focus on composites as opposed to single compounds	Do not know enough about bath surface reactions using inert anode technology M M • •	Lack of cost-effective screening performance tests • •	Lack of adequate control scheme for control of voltage and temperature
Metal contamination M M • • • • • • •		Lack of an accelerated test to predict long-term anode life •	Lack of thermal management systems • - inadequate insulation
Inability to achieve adequately high erosion characteristics at the frozen crust/electrolyte interface			Lack of a feed control system that eliminates anode effects
Operating environment - bath composition and other variables affect longevity of anode			Electrical connection to anode
			Lack of experience with multi-/bipolar operations - gas flow - current efficiency
			Material problems other than anodes for freezeless operation - lack of new container material
			Lack of consideration of design parameters outside of anode itself that could make the technology more viable
			Restraints of development based on targets - do not limit to retrofit

The environment in which the anode must operate presents a barrier to the anode's performance, particularly its longevity. Specific factors that must be addressed include bath composition, operating temperature, and maintenance of an adequate heat balance. The longevity of the inert anode material has been a problem during past efforts; at bench-scale, many materials have survived only on the order of hours. Although some materials have been developed with the potential to last five years or more, the metal contamination resulting from slow deterioration of the anode has been unacceptably high.

Metal contamination from dissolution of the anode in the bath is also a very critical barrier. The metal purity achieved in past research efforts involving inert anodes has been insufficient for current market needs.

Basic Knowledge

There are a number of fundamental issues related to the operation of non-consumable anodes that have not yet been fully investigated or resolved. This is due in part to a lack of models that would yield a better understanding of the overall process. One fundamental issue is that there has not been an adequate study to determine if the inert anode concept is truly worthwhile in terms of its potential for full-scale process improvement.

The most critical gap in basic knowledge is that not enough is known about bath surface reactions during use of the new technology. Having this information would enable the industry to incorporate some design principles into the anode. Another critical barrier is the lack of understanding of anode reaction responses to bath chemistry.

There is also little information on the activity of oxygen versus carbon dioxide under operating cell conditions, which prevents a complete understanding of the details of the electrolytic process using inert anodes. It is unknown, for example, whether oxygen will be so reactive that it might reduce current efficiency.

An expected reduction in the size of the bubbles associated with non-consumable anodes may reduce the forced mass transfer in the cell. This presents a challenge to operating the cell using a range of 2 percent to 3 percent dissolved aluminas.

Other gaps in the fundamental knowledge of non-consumable anodes exist in the following areas:

- knowledge of limiting current and rate-determining step
- knowledge of the ability of the anode to withstand penetration of nascent oxygen, aluminum fluoride, and cryolite, and the effect on the internal anode structure
- knowledge of ratio of thermal to electrical conductivity

Measurement/Evaluation/Analysis

The technology barriers in this category are mostly related to testing of the new anode materials. The most critical barrier is also perhaps the most fundamental, namely, that the industry has not yet evaluated the worthiness of the concept based on the best *extrapolated* (not available) technology. Other key barriers are the lack of adequately defined, cost-effective, screening performance tests for targets for candidate materials, and the lack of an accelerated test to predict the long-term life of a new anode material.

The cost and time of demonstrating a new material present significant hurdles to the development of inert anode technology. Past efforts have not tested materials sufficiently in continuous operation over long periods of time, which is critical to ensuring sufficient anode durability.

Systems

The technology challenges in the systems category range from lack of computer modeling to retrofitability issues. The lack of computer models that incorporate less-conventional materials and structures was identified as a critical barrier. Specifically, a well-developed, sophisticated tool (including a good, up-front simulation tool) is needed to simulate the total cell without having to build macro-scale test set-ups.

The lack of controls to regulate voltage and temperature and the lack of thermal management systems and materials for the cell were all cited as barriers. The most critical systems barrier was identified as the inability to keep the total cell voltage equal to or no worse than the situation in today's cells at the same current density. Total cell voltage must take into account all the IRs, the decomposition potential, the overvoltages, the bubble films, and compensation for the heat loss. This barrier is closely coupled with the lack of extensive computer modeling (see above).

Present aluminum feeding-control systems are another technical barrier because they do not eliminate anode effects. Inert anode technology itself is not enough to eliminate these disruptions. The electrical connection to the anode is yet another technology gap.

In addition to the problems with anode materials discussed earlier, other materials problems exist within the system, particularly for freezeless operation of the cell. If net energy efficiency is an essential goal, freezeless operation will be necessary. In this type of operation, the bath and the metal come into direct contact with the container. Currently, a freeze is used to protect the material, which automatically requires a very high heat transfer coefficient. In order to keep efficiency high, however, the freeze may have to be eliminated and additional material issues follow immediately (e.g., new container materials may be required to contain the electrolyte and make the system viable).

Another anticipated requirement for high system efficiency is multi-polar operation. Several technical barriers are associated with multi-polar/bipolar operation, particularly gas flows and current efficiency. These barriers are also related to the lack of adequate insulating materials.

The industry feels that there has not been enough consideration ("thinking beyond the conventional box") of design parameters apart from the anode that might make the anode itself more viable. An extreme example would be to produce aluminum at temperatures below its melting point; another possibility could be to keep the cell hot but cool the anode.

Finally, there are key systems barriers related to retrofitting new anode technology to existing cells (depending on costs and benefits). However, the development of inert anode technology should not be limited to retrofitting; there may be entirely new processes for using an inert anode technology that have not yet been discovered.

5 Technology Development Steps

Research on any new inert anode technology proposed will be expected to follow a pre-defined "pathway" to ensure that the development of a given technology does not continue if it is found to be technically and economically infeasible.

Exhibit 5-1 illustrates the chronological development steps of inert anode technology, including the critical components of each developmental step and the timeframe for completion of each phase of the work. The steps, which are discussed below in further detail, are

- comprehensive literature review and analysis,
- bench-top test,
- laboratory pilot test, and
- pilot test.

Economic analysis and modeling should be conducted following the paper analysis. This should be followed by increasingly more comprehensive economic analyses, particularly between the laboratory pilot test and the pilot test. More than one potential inert anode technology may be pursued at the same time. However, if a particular technology does not appear to be cost-effective, it could justify a decision to stop its development. A technical analysis should also be performed after each testing stage for each technology.

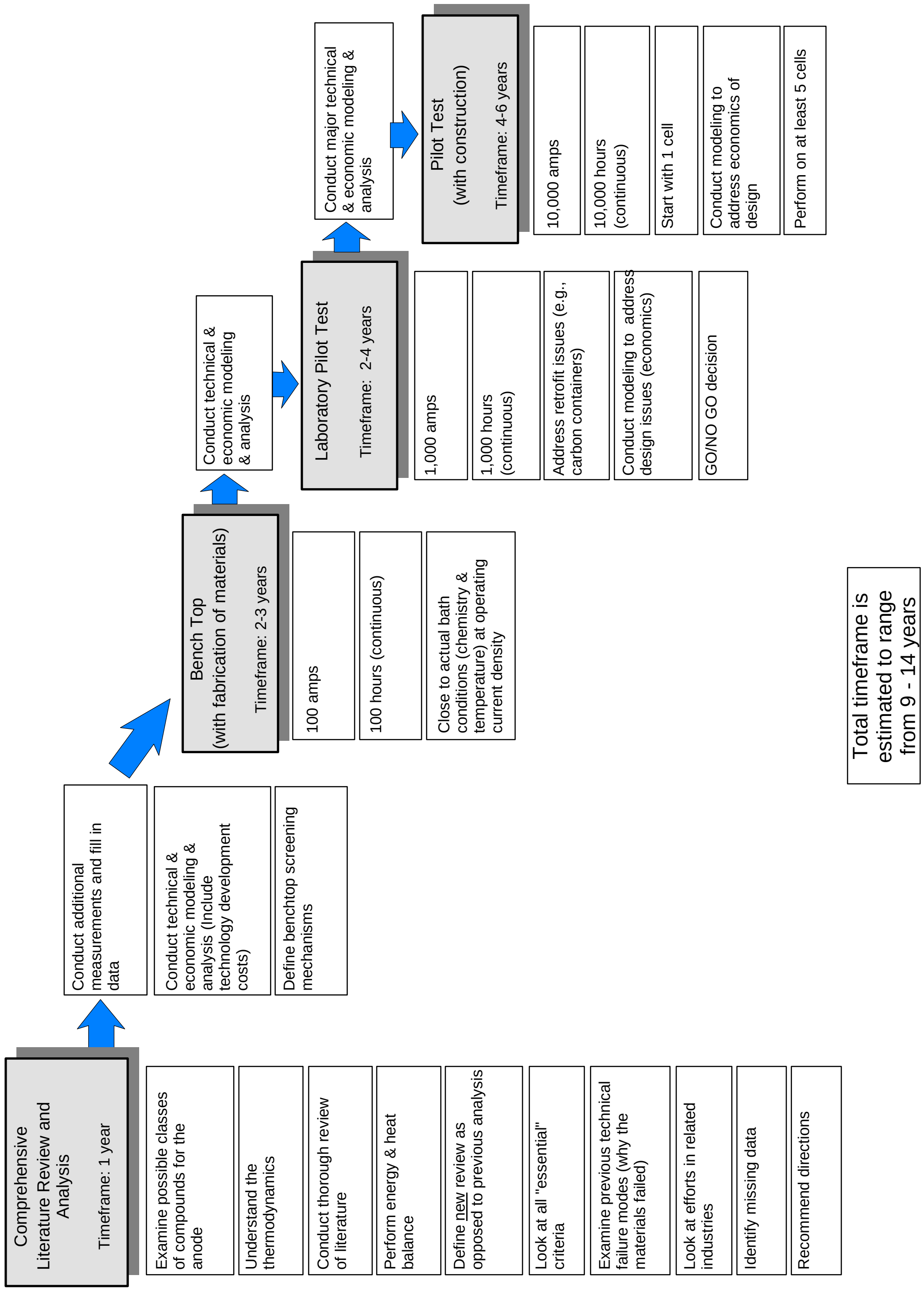
Comprehensive Literature Review and Analysis

The first and perhaps most critical step in the development of inert anode technology is a comprehensive literature analysis that it is anticipated the Department of Energy will initiate in the near future. It is hoped that this analysis will serve as a foundation and tool for proposers of future research in inert anode technology. The analysis will include the following:

- comprehensive literature analysis
- examination of past research efforts
- basic thermodynamic analysis
- identification of missing pieces of data

The literature review should be expanded to include an analysis of all the available material on anodes, including system design, voltage drop and rise, electron transfer, ionic interaction, metal ion displacement, oxidation resistance, and others. The analysis should look at the "essential"

Exhibit 5-1. Critical Steps Anticipated in the Successful Demonstration of an Inert-Anode Cell



criteria discussed in Section 3, although it is likely that these criteria will be refined and focused as more knowledge is gained. In examining reports of earlier thermodynamic analyses, and of materials investigated in the past, there should be a discussion of what failed and of what will be done differently in the present effort. In addition to this comprehensive literature analysis, individual proposers of specific technologies will need to perform an analysis of their own technology.

The thermodynamic analysis should cover every aspect of bench-top testing. Specific activities should include measuring the energy and heat balance of the system, projecting the fundamental properties of the system in the anticipated environment, and identifying classes of compounds potentially useful in inert anodes.

One result of the initial comprehensive analysis should be a better definition of essential targets; another could be a list of top potential candidate materials. The end product of a specific analysis should be an effort to convince the industry that the researchers have conducted an exhaustive study and are prepared to develop a unique and superior technology. They should present sufficient scientific data to give the industry a strong degree of confidence in the technology.

After the analysis, the industry and other stakeholders will determine if a technology is worth pursuing a step further. Several approaches might run in parallel for a time, with a decision to focus the effort at some later point. For example, four or five technologies might be supported at the bench- top level, which are reduced to two or three by the laboratory pilot scale, with a single technology supported at the pilot scale.

It is anticipated that the literature analysis will reveal that one or more pieces of critical data are lacking and that additional measurements are needed before the effort can proceed to a bench-top evaluation of a highly promising material.

A goal of this step is to develop recommendations for future research directions. Depending on the availability of data, they can be added to the literature analysis or may be determined before the bench-top testing begins.

Bench-Top Test

Research efforts selected for funding then would proceed to the bench-top testing stage. The major requirement here is that the anode be tested at 100 amps for 100 hours.

If the metal quality is found to be insufficient after this stage of testing, a decision will be needed on whether to continue the research or to change the criteria. It is possible that the criteria will change as more knowledge is gained; however, some decisions may have to be made on whether to relax some of these benefits.

Is there is a critical point at which the researchers should consider merging inert anode technology with wettable cathode technology? Clearly this question is also influenced by the technical progress in the wettable cathode area as well. Experience has shown that when technologies are combined, the chances of success go down dramatically, although the combination of these technologies could become the potential goal if the results of the bench-top testing are favorable. The analysis conducted earlier, as well as any newly measured data obtained between the literature analysis and the bench-top testing, should reveal any interactions that preclude one direction or another. (The economic analysis should include not only the economics of successfully operating inert anode technology, but also the cost of technology development.) After the bench-top testing is complete, researchers again should perform technical and economic analyses.

Laboratory Pilot Test

The laboratory pilot test of the inert anode must take place at 1,000 amps for 1,000 hours. The 1,000-hour test must be conducted continuously -- the test period cannot be broken down into eight-hour segments. Again, the "essential" criteria apply, although they may have been slightly modified by this point based on earlier results. Another technical and economic evaluation of the results will be required.

Pilot Test

The requirements for the pilot test are to operate at 10,000 amps for 10,000 hours. At first, the test should be performed using one cell at 10,000 amps. If the anode performs successfully, the test should be expanded to additional capacity.

A potential problem in testing cells containing multiple material components, especially at the pilot-scale level, is that there may be interference between different materials in the electrolyte bath. For instance, the presence of aluminum carbide in the bath, formed by reaction of the bath with the cell components, may interfere with the operation and thermodynamics of the oxygen-evolving anode. It is unknown at this time whether carbon will have to be kept out of the system to prevent its interference with the proposed inert anode material. There are potential problems with the use of carbon as a sidewall material depending on whether the inert anode is a retrofit to an existing cell. The goal is to avoid a retrofit situation that is carbonless unless absolutely necessary. This will be determined during testing.

Carbon anodes may have to be used in the pilot cell. However, several but not necessarily all of the anodes in the test cell should be inert anodes. It is also possible that a single plant-scale inert anode could be used and run at 10,000 amps.

Additional Development Steps

There are additional steps beyond the pilot testing stage, including the operation of multiple pilot cells and, finally, a full-size plant prototype. The inert anode should be run in an actual plant cell; if it works, the technology should be expanded throughout the entire plant. Before the inert anode technology becomes fully commercial, as much of the uncertainty as possible should be eliminated.

Retrofit Capability

Retrofit capability is a key issue with inert anode technology. If the new technology is technically and economically successful but ultimately cannot be retrofitted to existing cells, it will still be considered a success. However, the ability to retrofit would certainly be considered a major benefit, and would improve the technology's economics. Some of the issues pertaining to retrofit capability (e.g., use of conventional carbon liners or containers) should be answered well before the pilot test. Modeling will be extremely important in determining whether a retrofit requires a radically different design, if a technology is not worth pursuing, or if one technology is superior to another. Once a viable anode is demonstrated, modeling may also be beneficial in determining what kind of design might have an economic advantage, whether it can be combined with the wetted cathode, and what will be its interaction with other cell components (e.g., materials, walls, containers).

6 Next Steps

The aluminum industry will continue to be driven by the need to improve productivity as a means to lower production costs and remain competitive in world materials markets. A concerted industry effort to develop an inert anode by 2020 could play a key role in expanding the demand for aluminum products. By developing this framework for inert anode technology, the aluminum industry has taken a proactive step toward addressing competitive demands by focusing on technology that makes good business sense and responds to the need for environmentally responsible production.

Using this framework, the industry has focused on its most critical long-term technical need, the development of inert anode technology. It is anticipated that the framework will:

- Provide clear guidance on required technical performance to industry, universities, and national laboratories who are proposing new inert anode concepts

- Accelerate research into advanced electrolytic cell technologies by ensuring that the proposals received are more responsive to industry's needs

- Improve the efficiency of research efforts within individual companies by presenting a consensus on standardized performance, allowing them to direct their resources more appropriately

- Permit individual companies within any research consortia or partnerships that may be formed to allocate their resources more appropriately for research components not covered in the joint research

A likely first technical step would be the initiation of one or more of the comprehensive "paper" analyses discussed in Section 5. Beyond this, the North American aluminum companies need to consider the desirability of joint efforts in inert anode technology research, as well as possible mechanisms for funding and directing the research efforts. The industry also should consider the government's role in the overall effort to develop inert anode technology. Finally, the industry should consider examining other elements of advanced cell design that could complement inert anode technology and enhance its benefits.

A Roadmapping Participants

Bob Cheatham
Alumax, Inc.

Julian Copenhaver
Technical Manager
NSA - Div. of Southwire Company

Euel Cutshall
Laboratory Manager
Reynolds Metals Company

Subodh Das
Vice President, Technology & Quality
ARCO Aluminum, Inc.

Sara Dillich
Manager, Aluminum Processes
U.S. Department of Energy

John A. S. Green
Vice President, Technology
The Aluminum Association, Inc.

Rodney Hanneman
Vice President, Corporate
Reynolds Metals Company

Wayne Hayden
Manager, Engineering Materials Section
Oak Ridge National Laboratory

Jean-Paul Huni
Research Director
Alcan International Ltd.

Roger Johnson
Reduction Technology Specialist
Kaiser Aluminum & Chemical Corporation

Hank Kenchington
Aluminum Team Leader
U.S. Department of Energy

Richard O. Love
Technical Manager
Century Aluminum

Nolan Richards
Consultant

Ray Roberts
Northwest Aluminum Company

Bob Strieter
Director, Environmental Affairs
The Aluminum Association, Inc.

William Truckner
Director, Product Development
Aluminum Company of America

Paul R. Woodin
Technical Manager
Goldendale Aluminum Company

Ralph Woods
Manager, Ground Transportation
Kaiser Aluminum & Chemical Corporation